Evaluation of Liquidus in FeOx-SiO2 and FeOx-CaO Base Slags and Fluxes in Metallurgical Processes(FeOx-SiO2およびFeOx-CaO基の製錬スラグ、フラックスの液相面評価)

氏名	フロリアン　コンゴリ Florian　Kongoli
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論文審査委員	主査　東北大学教授　板垣 乙未生　東北大学教授　日野 光兀 東北大学教授　長坂 徹也

論文内容要旨

1. Introduction

The thermophysicochemical properties of slags and fluxes are of importance for controlling the smelting, converting and refining processes. Liquidus surface and viscosity are two important parameters of pyrometallurgical processes. They directly affect the overall efficiency of the process and the quality of the products. However, the data on these properties are still lacking. Hence, the present study was undertaken with the following objectives: (a) quantification of effect of the oxygen potentials on the liquidus surface of FeO_X-SiO_2 and FeO_X-CaO base slags, (b) quantification of the effect of several fluxing components on the liquidus surface of FeO_X-SiO_2 and FeO_X-CaO base slags, and (c) clarification of some disputable discrepancies between the results which have been reported in literatures concerning the effect of oxygen potential and several fluxing components on the liquidus temperature and the viscosity of slags and fluxes. Based on the present results, the important implications in some pyrometallurgical processes were discussed.

2. Development of modeling and methodology for evaluating liquidus surface

Following the previous works on the thermodynamic modeling for some complex sulfide systems, the methodology for evaluating the liquidus surface in the oxide systems was

developed and employed in the present study, which consists in the construction of new types of liquidus surface diagrams that correctly simulate the slag behavior in various pyrometallurgical processes and give unequivocally the effect of fluxing components and oxygen potential on the liquidus surface. These diagrams were constructed based on the new thermophysical modeling of the slag that adequately reflects the physicochemical properties and has reliable prediction ability. This ability was validated through a detailed comparison of the model predictions with the existing experimental data especially at intermediate oxygen potentials between log P_{O_2}/atm = -10 ~ -5 where most of nonferrous pyrometallurgical processes are operated. Hence, the validation was in fact one of the main important points in this study.

It was shown that the model prediction for the effect of P_{O_2} and fluxing components of Al_2O_3, MgO and Cu_2O on the liquidus surface in the FeO_X-CaO-SiO_2 system at 1300℃ agree very well or within the experimental error and uncertainty with the existing data. This gives confidence on the prediction ability of the model which is used for the construction of the new types of the diagrams.

3. Construction of new types of diagrams

It was shown that the way of representing multicomponent liquidus diagrams is of considerable importance if correct conclusions need to be drawn about the thermophysicochemical properties of the slags and the effect of fluxes and minor components. Several new types of diagrams were introduced which are special combinations of new concepts of presentations. These are related to the oxygen potential (diagrams given at constant P_{O_2}, constant CO_2/CO and/or in equilibrium with another liquid phase), to the special dimensions (diagrams given as a function of Fe/SiO_2 or Fe/CaO ratio and one other component and/or at a constant content of one component if more than four components are present) and to the temperature (polythermal and isothermal diagrams).

The liquidus surface at a constant oxygen potential in the FeO_X-SiO_2 and FeO_X-CaO base slags was evaluated in the polythermal and isothermal diagrams. The liquidus surfaces of FeO-Fe_2O_3-SiO_2-CaO system at 10^{-8} atm were given in the forms of CaO versus Fe/SiO_2 ratio or SiO_2 versus Fe/CaO ratio. It was demonstrated that these diagrams can present very clearly the effect of fluxing components of CaO and SiO_2 in the FeO_X-SiO_2 and FeO_X-CaO base slags, respectively. The liquidus surfaces in the multi-component FeO-Fe_2O_3-SiO_2-CaO-Al_2O_3-MgO slags also could be successfully expressed in the form of fluxing component (Al_2O_3 or MgO) versus Fe/SiO_2 or Fe/CaO with a given CaO or SiO_2 content.

A special thermodynamic interpretation was dedicated to the diagrams at a constant CO_2/CO ratio as well as the diagrams saturated with another liquid phase. It was shown that the slag liquidus surface at a constant CO_2/CO ratio is a convenient way for describing the slag liquidus surface and the effect of minor components in those processes, such as slag solidification, where the oxygen potential changes continuously. It could describe more

dynamically the effect of oxygen potential and clarify the relation between the CO_2/CO ratio and the oxygen potential in terms of the liquidus surface. The analysis of the variation of P_{O2} and CO_2/CO showed that, during slow equilibrium cooling although the oxygen potential changes continuously, the CO_2/CO ratio stays almost constant. Consequently, this new type of diagrams at a constant CO_2/CO ratio also could simulate the slow cooling process of the industrial slag.

4. Effect of oxygen potential on phase relations and liquidus surface

The liquidus surface of FeO-Fe_2O_3-SiO_2-CaO system has been studied so far in equilibrium with metallic iron or in air and the data at intermediate oxygen partial pressures are missing. Hence, the effect of oxygen potential, ignored until that moment in all pyrometallurgical processes, was quantified for the first time and properly analyzed in the present study. The several diagrams were given for both FeO_X-SiO_2 and FeO_X-CaO base slags as well as iron sintering materials which unambiguously show the important effect of oxygen potential on the liquidus surface. It was found that a change of P_{O2} can totally change the phase relations and the slag liquidus surface. It was also found that fayalite may not exist at some intermediate oxygen partial pressures, making the name "fayalite slag" totally irrelevant. It was suggested that the effect of P_{O2} is not uniform and should not be generalized since it depends on the particular set of conditions such as the slag composition, minor components etc.

The effect of CO_2/CO ratios and oxygen potentials on the liquidus temperature were also quantified and the contradictions often found between the microscopic results of laboratory quenching measurements and slowly cooled solidified smelting slags from the industrial practice were clarified. It was shown that there is a fundamental difference between the quenching and slow equilibrium cooling of an iron oxide slag at intermediate oxygen potentials in terms of the primary precipitate phases, the effect of minor components, the mineralogical composition of the solidified slag, etc. The constructed diagrams at a constant CO_2/CO ratio shed light in the understanding of the slag solidification process and the solidified slag mineralogy, which are recently becoming important in the environmental point of view.

5. Effect of fluxing components on liquidus surface

The effect of several fluxing components such as Al_2O_3, MgO and Cu_2O on the liquidus surface in the FeO-Fe_2O_3-SiO_2-CaO base slags has been quantified through the use of new types of polythermal and isothermal diagrams. A detailed analysis has been carried out for each component and the most important points on the effect of each of them have been highlighted.

The effect of Al_2O_3 on the liquidus temperature at P_{O2} of 10^{-8} atm and several Fe/SiO_2 ratios was evaluated. It was found that, in the low CaO region corresponding to "fayalite" slag, the liquidus temperature on the spinel surface increases by 6-8 degree per positive % increment of Al_2O_3. At a high CaO region, however, nearby Ca_2SiO_4 saturation, the effect of Al_2O_3 was not significant, and the difference in the liquidus temperature between Fe/SiO_2

= 1.1 and 2.3 was not considerable. However, in coexistence with metallic iron, the liquidus temperature decreased on the olivine surface by addition of Al_2O_3. As for the effect of MgO, it was found that MgO in some cases stabilizes the spinnel phase and decreases significantly the liquid region, but in another case MgO suppresses the formation of solid silica. It has been found that the effect of each of these fluxing components on the liquidus surface is far from being uniform. Their effect could not be generalized since it was specific for a specific set of conditions. It was also pointed out that the effect of the same fluxes can be different not only quantitatively but also qualitatively between the conditions in the oxidative and reductive processes.

6. Implications of the present results in pyrometallurgical processes

The direct implications of the results of present work in the pyrometallurgical processes have been demonstrated in two directions : (a) in developing new smelting and processing technologies, and (b) in evaluating and optimizing process parameters and operating conditions in the existing processes.

The following examples have been described and discussed.

(1) Availability of the newly proposed "ferrous calcium silicate" slag in copper continuous converting. It was found that the new diagrams presented in the present work could quantify in an unambiguous way the liquidus surface of this slag and the effect of oxygen potential and minor components and consequently its availability in copper smelting processes.

(2) Optimization of iron ore sintering "slags" in order to avoid the early meltdown in the blast furnace. It was found that the oxygen potential and the minor component play a considerable role in creating or eliminating the conditions of early meltdown in the blast furnace.

(3) Optimization of the slag viscosity through the quantification of the liquidus surface and its close relation with the viscosity. The effect of several factors such as oxygen potential, Fe_2O_3 and Fe/SiO_2 ratio were clarified, and it was found that the effect of fluxes on the viscosity of the slag should be considered in close relation with the slag liquidus temperature otherwise wrong conclusion may be drawn. Contrary to a long time incorrect belief, it was given in the present study that, at a certain set of conditions, a particular component may be a good flux in term of the liquidus temperature and a bad one in terms of the viscosity. It was also clarified that the effect of a flux on the viscosity and the liquidus temperatures is not uniform and should not be generalized.

(4) Evaluating the process parameters and operating conditions in various pyro-metallurgical processes. It was found that the quantification of the liquidus temperature and the viscosity are of very importance for smelting processes and the use of new diagrams presented in the present study makes very effectively the proper quantification of these slag properties.

論文審査結果の要旨及び学力確認結果の要旨

論文提出者氏名	Florian Kongoli
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論文審査及び学力確認担当者	主査　教授　板垣　乙未生　　教授　日野　光兀 教授　長坂　徹也

論文審査結果の要旨

酸化鉄を主成分とするスラグやフラックスの溶融温度は乾式製錬の工程管理の基本データとして重要であるが、非鉄金属の硫化鉱製錬で対象とされる 10^{-10}~10^{-5} 気圧の酸素分圧域での液相面温度は殆ど知られていない。本研究は、計算熱力学の手法を用いて、FeO_X-SiO_2 および FeO_X-CaO 基スラグの液相面温度に及ぼす酸素ポテンシャルと添加成分の影響を体系的に明らかにしたもので、全編7章からなる。

第1章は緒論であり、本研究の意義と目的について述べている。

第2章では、スラグの状態図構築用の計算熱力学モデルを開発し、FeO_X-SiO_2, FeO_X-CaO, CaO-SiO_2 各2元系、FeO-Fe_2O_3-SiO_2-CaO4 元系、FeO-Fe_2O_3-SiO_2-CaO-$Al_2O_3$5 元系などの実測状態図データと比較することによって、本モデルの適用性を検証している。

第3章では、FeO-Fe_2O_3-SiO_2-CaO 系や FeO-Fe_2O_3-SiO_2-CaO-X(X:Al_2O_3, MgO, Cu_2O)系などの多元系スラグの液相温度を2軸平面上で簡潔に書き表す方法について検討し、等酸素ポテンシャル図、等温図、(%Fe/%SiO_2)組成比相関図、(%Fe/%CaO)組成比相関図などを多面的に用いることによって、液相温度の系統的評価が可能となること、スラグ状態図の工業利用において優れた利便性があることなどを示している。また、(P_{CO}/P_{CO_2})分圧比相関図を用いて、多元系スラグの凝固経路を明らかにすることに成功している。

第4章では、FeO-Fe_2O_3-SiO_2-CaO 系スラグの液相面および相関係に及ぼす酸素分圧の影響を検討し、酸素分圧が増大するとスラグの(%Fe^{3+}/%Fe^{2+})組成比が増加する結果、液相面および相関係が大幅に変化すること、ファヤライトと従来呼称されているスラグ相が 10^{-9} 気圧以上の酸素分圧域では存在しないことなどを明らかにしている。また，これらの結果に基づき、非鉄製錬操業の妨害因子となるマグネタイト相の析出防止策を提示している。

第5章では、FeO-Fe_2O_3-SiO_2-CaO 基スラグの液相面に及ぼす Al_2O_3, MgO, Cu_2O などの添加成分の影響を系統的に評価し、酸素分圧やスラグ中の CaO 濃度などによって添加成分の影響が顕著に異なる場合があるので、個別の条件での検討が不可欠であることを示している。

第6章では、本研究で構築された FeO_X-SiO_2-CaO 系スラグの状態図に基づいて、フェラスカルシウムシリケート系の新しい銅製錬スラグの提唱、焼結工程における鉄鉱石の早期融解現象の検討、スラグの粘性に関する考察などを行い、スラグやフラックスの液相面データの工業利用について述べている。

第7章は、本研究の全体から得られた結果の総括である。

以上要するに本論文は、酸化鉄を主成分とするスラグおよびフラックスの液相面を酸素分圧や添加成分などの影響を含めて体系的に評価し、乾式製錬におけるスラグ制御およびフラックス利用の指針について考究したもので、金属工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。

学力確認結果の要旨

平成15年11月17日、審査委員ならびに関係教官出席のもとに、学力確認の試問を行なった結果、本人は金属工学に関する十分な学力と研究指導能力を有することを確認した。

なお、外国語に対する学力も十分であることを認めた。

審査結果の要旨

酸化鉄を主成分とするスラグやフラックスの溶融温度は乾式製錬の工程管理の基本データとして重要であるが、非鉄金属の硫化鉱製錬で対象とされる 10^{-10}~10^{-5} 気圧の酸素分圧域での液相面温度は殆ど知られていない。本研究は、計算熱力学の手法を用いて、FeO_X-SiO_2 および FeO_X-CaO 基スラグの液相面温度に及ぼす酸素ポテンシャルと添加成分の影響を体系的に明らかにしたもので、全編7章からなる。

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